MECHANICAL, THERMAL, AND MOISTURE ABSORPTION PROPERTIES OF NANO-CLAY REINFORCED NANO-CELLULOSE BIOCOMPOSITES

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Abstract: *In this research, fully environment-friendly, sustainable and biodegradable 'green' composites were fabricated. A novel material comprised of microfibrillated cellulose (MFC) and laponite clay (LC) with different inorganic/organic ratios (m/m) was prepared. The composites characterized by different techniques namely; Tensile, bending, dynamic mechanical analysis, and water absorption tests. The morphologies of these nanocomposites were evaluated through scanning electron microscopy (SEM). Results showed considerable improvement of mechanical properties; specifically in elastic modulus, tensile strength and flexural modulus with addition nanoclay up to 7.5 wt% nano-clay. However, with an increased load of clay in the nanocomposite, the mechanical properties decreased due to the agglomeration of excessive nanoclay. The storage modulus was significantly increased with addition nan-oclay at high temperature.*

1. Introduction

In recent years, organic/inorganic composites with reinforcement on the nanometer-scale have attracted great interest from researchers. One of the most promising composite systems is hybrids based on organic polymers and inorganic clay minerals consisting of a layered structure. Compared to their micro- and macro counterparts and the pristine polymer matrix, polymer/clay nanocomposites (PCN) exhibit dramatically improved mechanical, thermal and barrier properties.

Cellulose is probably the most abundant and renewable biopolymer. Each year ~100 billion metric tons of cellulose is produced. Recently, a large amount of work has proven that natural fibers, also referred to as cellulosic fibers, can be an alternative to inorganic/mineral based reinforcing fibers in commercial composite materials. Natural fibers have many advantages, such as renewability, abundance, low density, biodegradability, and last but not least, low cost. Despite this, the applications of these lignocellulosic fillers are still limited in industrial practice, in part due to their poor mechanical properties in general— although they have good specific mechanical properties given their low density [1].

Recent and ongoing research on polymer/inorganic nanocomposites has shown dramatic enhancements in stiffness, strength and thermal properties over those of polymers, without compromising on density, toughness or processibility [2].

Research to date has shown that polymer/clay nanocomposites offer enhanced thermomechanical properties with inexpensive raw materials and not very involved processing procedures Nanoclays have a high aspect ratio and a plate morphology compared to micro-scale fillers which, together with their low cost and low content level required, would make them efficient as filler reinforcements. However, only a few investigations have been reported on the mechanical properties of polymers after the addition of nanoclays, particularly for natural matrix [3]. However, several considerations have to be taken into account in the design of natural fibers composites. One of the most important issues is the degradation behaviors of the composites exposed to environmental conditions such as humidity, sunlight or microorganisms. The poor resistance of the fibers to water absorption can have undesirable effects on the mechanical properties and the dimensional stability of the composites [4]. Therefore, it is important to study in detail the water absorption behavior in order to estimate not only the consequences that the water absorbed may have, but also how this water uptake can be minimized in some way. Many attempts are being made to improve the properties of natural fibers such as bacterial cellulose membrane by nanoclay reinforcement [5,6].

In this work, composites in film form made entirely from natural resources were prepared using clay as the reinforcing phase and MFC as the matrix. The objective of this work was to determine the thermal, mechanical and water absorption property improvement attainable by combining a biobased reinforcement with a biobased matrix; to examine the reinforcing effect of nano-clay as a reinforcement in nano-web like MFC.

2. Experimental

2.1 Materials

The micro fibrillated cellulose, used in this study as matrix, is Celish R- KY-100G, MFC made from highly refined and purified wood pulp, supplied by Daicel Chemical Industries, Ltd., Japan. MFC was obtained by a homogenizing process on kraft pulp consisting of 50% lodge pole pine, 40% of white spruce and 10% of Douglas. The Celish R-KY-100G pulp is composed of water of 90% in weight, bears a temperature up to 200^{o}C and the cellulose nanofibre diameter ranges from 10 nm up to 100 nm. Nano-clay, hydrophilic bentonite, supplied by sigma Aldrich, Japan

2.2 Specimen preparation

Microfibrillated Cellulose was diluted with water at fibre content 0.2%, and then stirred for 2 hours. CL 2.5, 5, 7.5, 10, 30, 50 wt% were added to water during stirring process. The mixture was filtered by vacuum pump for one day. The filtered MFC sheet is sandwiched between two metal plates in a vacuum oven for two days at 75^{o}C under low pressure. The dried sheet pressed in hot press under 100Mpa at 160^{o}C for 5min. This compressing pressure was established based on a previous study by Nakagaito and Yano [7] in which 100MPa yielded the best strength values for MFC-based composites.

2.3 Tensile and bending tests

The tensile properties of samples were measured using a Shimadzu Autograph universal testing machine. The specimen gage length was 20mm and the testing speed was set to 1mm/min. The specimen dimension was 40x5x0.5 according to JIS K7073 (1988), sand paper

tabs were attached at both ends of specimen by adhesive. Flexural properties were measured according to JIS K 7074. Three point bending tests were conducted at room temperature. Dimensions of the specimen for the bending test were 1.5mm in thickness, 5mm in width and 40mm in length. The span was set to 34mm. At least five samples for each material were prepared. Bending strength and bending modulus were determined.

2.4 Dynamic mechanical analysis

Seiko DMS 6100 instruments with a chuck distance of 20mm was used to perform the DMA studies in order to evaluate tanδ and T_g. DMA gives both storage modulus and loss modulus characteristics as a function of temperature. The measurements were carried out at a heating rate of 2°C/min from 30°C to 250°C at fixed frequency of 1 Hz. The samples were rectangular bars of sizes 40mm×5mm×0.5mm.

2.5 Water Uptake

Water uptake was carried out by making samples of 40mm × 5mm × 1mm. The samples were kept at 95% RH for 48h and increase in weight was taken as final weight (Wt). All specimens were weighed using electronic balance with an accuracy level of 0.001 digits. The water content (Wc) in the sample was measured as % weight increase in the sample. Eq. (1) is used to calculate the water content Wc in the specimen.

$$Wc = \frac{Wt - Wo}{Wo} x100 \qquad (1)$$

where Wt is the weight of specimen at time *t* and *Wo* is the initial weight of the sample before placing in water

2.6 Scanning electron microscopy observations

FE-SEM was used to observe the surface of MFC composite. Fractured surfaces of the specimens failed by tensile test were examined by scanning electron microscopy (SEM) using JSM-7001FD equipment. Prior to SEM observation, all samples were sputter coated with a thin layer of gold to avoid electrical charging. SEM used also for examination of surface microstructure of all composites before and after one week UV-irradiation.

3. Results

3.1 Tensile and Flexural properties

The tensile strength and elastic modulus the nano-clay filled MFC composite series is shown in Fig. 1.

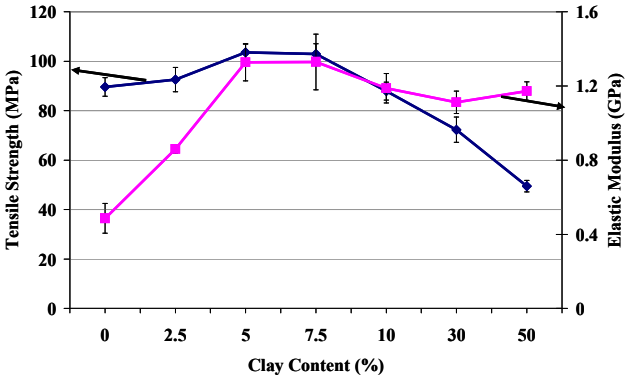

Figure 1. Tensile strength and elastic modulus for MFC composites with different contents of nano-clay

It can be seen that the addition of nanoclay in the composite affect the tensile strength as well as elastic modulus. The tensile strength was slightly increased up to 5 wt% of nano-clay. The elastic modulus was increased significantly from 0.48GPa for neat MFC to 1.33GPa for 7.5wt.% nanoclay. However, the tensile strength and elastic modulus were decreased continuously as nanoclay content increases, to be discussed later.

The flexural strength decrease gradually with increasing nano-clay content whereas the flexural modulus increase up to 7.5wt% of nano-clay then decrease with increasing the nano-clay content. It is worth noting that flexural modulus increased significantly from 3.4GPa for neat MFC to 4.6GPa at 7.5wt% of nano-clay as shown in Fig.2. From this result, it is also observed that the improvement of the tensile strength as well as the flexural modulus of composites with nano-clay is due to the exfoliation/intercalation of nanoscale clay particles in the matrix which restricts the mobility of polymer chains under loading. The orientation of clay platelets and polymer chains with respect to the loading direction can also contribute to the reinforcement effects; however, the decreasing rate of tensile strength with higher clay content is due to the presence of excess unexfolifated/intercalated aggregates. The decreased mechanical properties of those nanocomposites are possibly also due to the excessive nano particle clay that was not well dispersed in the polymer. The agglomerated nanoclay created stress concentrations in the polymer matrix and therefore decreased the tensile strength and elongation at break; the poor bonding between the polymer chain and the agglomerations of nanoclay decreased the elastic modulus [8]. The nanoclay acts as a crack arrestor during loading by inducing deformation mechanisms such as crack pinning and debonding which results in the specimen failing under deformed condition. The lower values of strength and strain is due to the agglomeration at higher clay (10 up to 50wt.%) concentration.

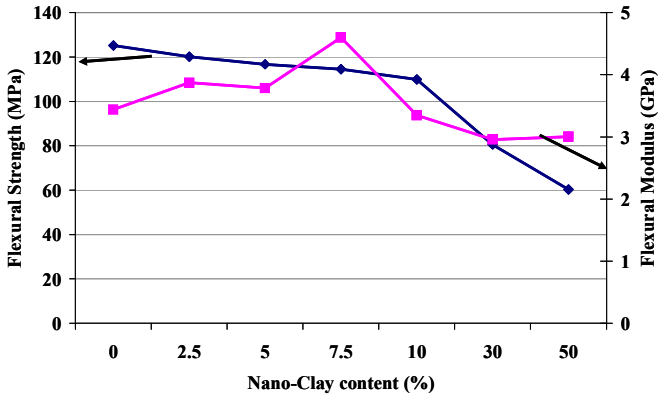

Figure 2. Flexural strength and modulus for MFC composites with different contents of nano-clay

3.2 Dynamic mechanical analysis

The effect of the addition nano-clay into MFC film on the thermal mechanical behavior was investigated with DMA at nano-clay content of 0, 2.5, 5, 7.5, 10, 30, 50 wt.%. The evolution of the storage modulus E′ as a function of temperature is reported in Fig. 3.

The storage modulus for the MFC film is much higher than the typical 1 GPa range for isotropic polymers, and decreases gradually with increasing temperature. The curve for neat MFC matrix shows a gradually decrease E′ value around 14.3 GPa at 30 °C, 7.9GPa at 200 °C, which corresponds to the main α relaxation associated with the glass-rubber transition. There is a noticeable decrease in the storage modulus at low temperatures with the addition of high content of nan-caly in MFC matrix. The storage modulus at 30 °C for 50 wt % nano-clay/MFC film is 10.9 GPa compared to 14.3 GPa for the neat MFC film. The E′ at 200°C increased significantly from 7.9 GPa for neat MFC to 9 GPa for 7.5 wt.% nano-clay. At room

temperature, the tan δ is around 0.04, which is comparably high and favorable in the context of acoustic membrane applications. The shapes of tan d curves for the different composites were similar, but the MFC film (Fig. 4) showed a different behavior. For films containing nano-clay, the damping remains constant, and then increase at different temperature.

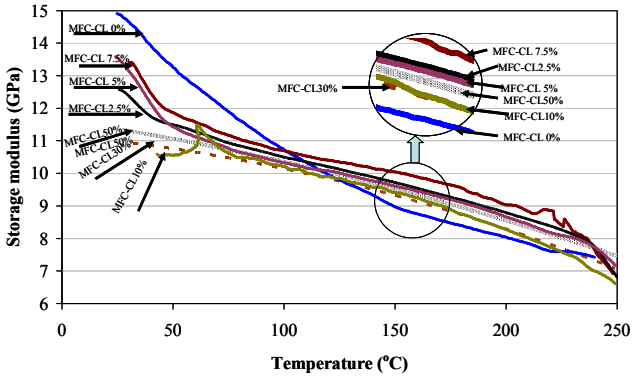

Figure 3. Storage modulus for MFC composites with different contents of nano-clay

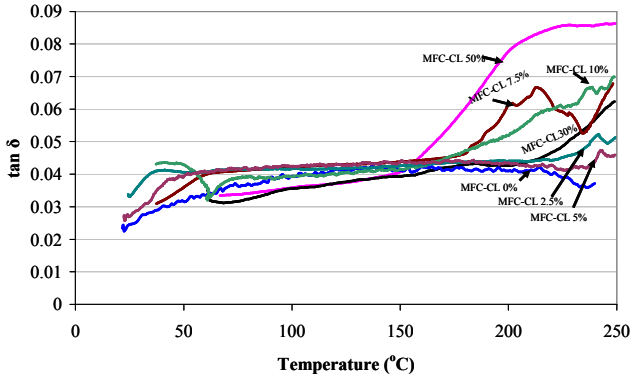

Figure 4. tanδ for MFC composites with different contents of nano-clay

3.3 Water uptake

Moisture sensitivity of MFC-based material is a key challenge towards the substitution of traditional plastics for commodity, most precisely, for packaging applications. The water uptake of composites during the exposure at R.H. 95% was evaluated for 48 h (see Fig. 5). MFC films showed slight higher moisture sensitivity than other samples modified by 2.5, 5, 7.5 wt.% nano-clay. Due to the hydrophilicity of the MFC matrix, the chain mobility increases at room temperature by breaking the attraction forces in the host matrix and a consequent increase in concentration of exposed moisture-sensitive hydroxyl groups, facilitating diffusion of water molecules throughout the polymer matrix. After mixing with clay, an overall decrease in hydrophilicity was expected, regardless of the clay concentration in the systems. The presence of barriers in the form of torturous paths of clay could generate difficulties in diffusion through the matrix [9]. The MFC-CL2.5 showed a little lower moisture sensitivity than MFC, which was due to the hurdles in the way of moisture because of clay presence. The concomitant decrease in water resistance in the case of MFC-CL30and 50, must be attributed to the poor dispersion of fillers which could result in a lower engagement of OH groups with layers, making them more available for moisture absorption.

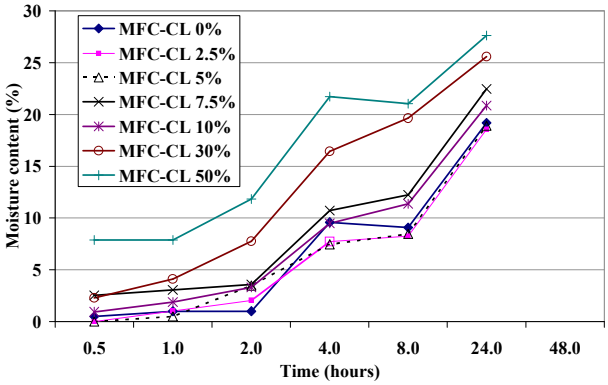

Figure 5. Moisture content for MFC composites with different contents of nano-clay

3.4 Scanning electron microscopy observations

In Figure 6a, a surface micrograph of a fibrous nanofibril network film is presented. A fine weblike, and highly fibrous network structure, is apparent, consisting of nanofibrils. The typical lateral dimension is 10-300 nm. This indicates that the individual nanofibrils most often consist of cellulose microfibril aggregates rather than smaller individual microfibrils. The nanofibril length is several micrometers and nanofibril ends are not apparent. Furthermore, individual nanofibrils are swirled and physically entangled with respect to each other. The predominant orientation appears to be random-in-the-plane. Because films were prepared from water suspensions, strong secondary interfibril interaction including hydrogen bonds was expected. No difference in average nanofibril width could be observed for the different samples studied. On the other hand, Laponite particles are well known by its plate-like shape, around 30 nm in diameter [6] and, due to its small size, clay particles can easily penetrate inside the cellulose matrix, keeping a close interaction with the polymer. The layered structure is apparent in Figure 6b. The fibrillar nature of the material is also apparent in the fracture surface presented in Figure 6b-6h. Perhaps the most important structural characteristic is that the nanofibrillar films are porous. The nature of the porosity and its extent is of obvious significance to physical properties. The pores are irregular in shape, as expected in a high-density network, and a considerable amount of porosity is apparent in Figure 1a. The typical pore diameter is in the range 10-150 nm (Figure 6a). Fig. 6g, and 6h show the presence of excess unexfolifated /intercalated aggregates. The decreased mechanical properties of those nanocomposites are possibly due to the excessive nano particle clay that was not well dispersed in the polymer.

Conclusion

MFC/nanoclay composites were prepared with the addition of nanoclays at 2.5, 5, 7.5, 10, 30, and 50 wt.% concentrations. The effect of nanoclay on the mechanical properties was studied. The results showed considerable improvement of mechanical properties; specifically in elastic modulus, tensile strength and flexural modulus with addition nanoclay up to 7.5 wt% nano-clay. The modulus of elasticity increased significantly by about 173% at 5, and 7.5 wt. % nanocaly. The flexural modulus increased by about 26% at 7.5wt% nanoclay. However, with an increased load of clay in the nanocomposite, the mechanical properties decreased due to the agglomeration of excessive nanoclay. The storage modulus was significantly increased by about 14% at200^{o}C at 7.5wt% nanoclay. Based on the results, it may be concluded that nanoclay can be successfully used as filler at low loadings content that provides good

mechanical and water barrier properties and hence improves the properties that are likely to be affected by water or moisture content namely tensile, Tg and flexural properties.

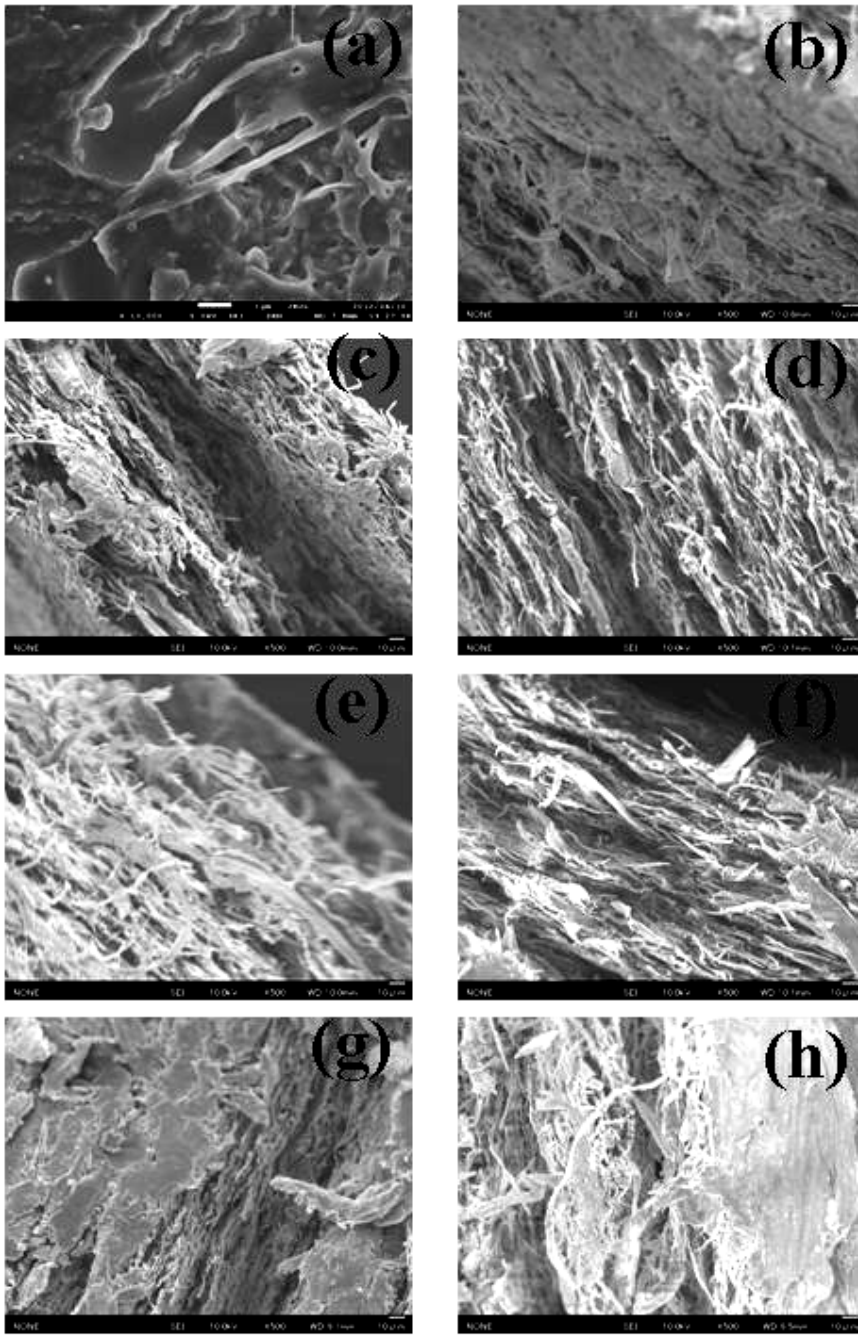

Figure 6. FE-SEM observation for (a) MFC, SEM observation for; (b) MFC-CL 0%, (c) MFC-CL 2.5%, (d) MFC-CL 5%, (e) MFC-CL 7.5%, (f) MFC-CL 10%, (g) MFC-CL 30%, and (h) MFC-CL 50%.

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